

Claims 2-4, 6 and 8 have been rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent No. 5,888,258 to Kaaber in view of U.S. Patent No. 6,139,990 to Kubota et al.

Claim 5 has been rejected under 35 U.S.C. 103(a) as being unpatentable over Kaaber in view of Kubota as applied to claim 3 above, and further in view of U.S. Patent No. 3,837,583 to Kugelberg et al.

Claim 7 has been rejected under 35 U.S.C. 103(a) as being unpatentable over Kaaber in view of Kubota as applied to claim 4 above, and further in view of U.S. Patent No. 5,421,524 to Haddow.

Claims 15-17 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Kaaber in view of Kubota as applied to claim 2 above, and further in view of WO 02/098795 to Kanbara et al (Kanbara).

Each of the above four rejections are based on the teachings of Kaaber as a primary reference and Kubota et al as a secondary reference.

Applicants submit that Kaaber and Kubota et al do not disclose or render obvious the presently claimed invention and, accordingly, request withdrawal of these rejections.

The present invention, as set forth in independent claim 2, is directed to a method for producing roundish fused alumina particles, wherein the roundish fused alumina particles have a mean particle size of 5 to 4,000 μm and a roundness of 0.85 or more, wherein the method comprises removing edges of fused alumina particles by making the fused alumina particles collide with each other. The roundish fused alumina particles of the present invention exhibit a large thermal conductivity.

The method of the present invention produces roundish “fused alumina particles” by removing edges of fused alumina particles by making the fused alumina particles collide with each other.

As discussed in the Amendment Under 37 C.F.R. § 1.111 filed on September 11, 2009, fused alumina particles, which are used as a raw material in the method of the present invention for producing roundish fused alumina particles, are virtually single crystal particles, as disclosed at page 2, lines 25 to 27, and page 7, lines 9 and 10 of the present specification, and are generally produced by the method comprising the following steps:

- (a) fusing a calcined alumina in an electric furnace at about 2500 to 3000°C;
- (b) pouring the fused alumina into a vessel and cooling it therein to obtain an alumina ingot; and
- (c) crushing the alumina ingot, e.g., by a jaw crusher, a roll breaker, and the like to form fused alumina particles.

Since fused alumina particles, which are used as a raw material in the method of the present invention for producing roundish fused alumina particles, are virtually formed of single crystal, when the fused alumina particles are collided with each other, e.g. by a jet mill, so-called “pulverization” of fused alumina particles hardly occurs, and rather the characteristic edges of the fused alumina particles are broken. See page 7, lines 9 to 21 of the present specification. Accordingly, the number of sharp edges of the fused alumina particles is reduced, and roundish fused alumina particles having no sharp edges are finally obtained.

Since the roundish fused alumina particles obtained by the method of the present invention are virtually single crystal particles, rather than polycrystalline particles, they exhibit a large thermal conductivity. See page 2, lines 25 to 27 of the present specification.

Kaaber relates to a grinding aid for use in an abrasive material, wherein the grinding aid consists of fluoride-containing inorganic compounds such as cryolite (Na_3AlF_6), which is obtained from a "cold bath" which is described at column 3, lines 26 to 42 of Kaaber.

In Kaaber, as disclosed in the Abstract, the grinding aid is produced by a method wherein the cold bath is crushed, optionally in several steps, whereby particles of an optional free metallic aluminium residue are rolled to flakes, following which the crushed material is screened to optionally sort out the formed aluminium flakes, and then the residual material is recovered as a product or is optionally subjected to further grinding and optionally screening to provide a material which preferably has a grain size distribution corresponding to 100% by weight less than 100 micrometers. This grinding aid lends itself for use in the product of abrasive materials.

As applicants have previously argued, Kaaber does not disclose grinding fused alumina particles with use of a jet mill. The Examiner has not specifically responded to this argument. Applicants believe the Examiner may not understand that there is a difference between the alumina disclosed in the Examples of Kaaber and the fused alumina that is employed in the present invention.

In the present Office Action, the Examiner states at page 6 as follows:

Regarding the argument for claim 2, Kaaber discloses using a jet mill to reduce the size of alumina particles to the size of no more than 100 gm (see examples 2 and 5).

Applicants submit, however, that Kaaber does not disclose using a jet mill to reduce the size of alumina particles, and more specifically does not disclose milling alumina particles.

Applicants submit that it is clear that Kaaber discloses milling a "cold bath" which mainly contains cryolite and chiolite and may contain a small amount of alumina as an impurity. Therefore, Kaaber does not disclose milling alumina particles.

In support of the above, applicants refer the Examiner to the following descriptions of Kaaber:

1. A grinding aid comprising particles of crushed cold bath, said cold bath being the residual solidified content of an electrolysis cell ... which comprises an acid mixture of an aluminum fluoride, chiolite and cryolite. (Kaaber, Claim 1)

4. A grinding aid according to claim 1, in which the cryolite and chiolite content is at least 75% by weight. (Kaaber, Claim 4)

The problem underlying the invention is to provide a grinding aid which is suitable as substitute for the finely ground, naturally occurring, neutral cryolite used previously, and which does not exhibit the above-mentioned drawbacks associated with the use of synthetic cryolite, a method of producing it, use of it for producing abrasive materials, and abrasive materials containing it. (Kaaber, Column 3, lines 1 to 7)

The alumina referred to in Example 1 of Kaaber, which is used in Examples 2 and 5 of Kaaber, is not the same as the fused alumina used in the present invention, since the "cold bath" used in the examples of Kaaber contains a large amount of cryolite and chiolite and a small amount (2.3 wt%) of alumina as an impurity.

Further, as discussed above, a fused alumina is an alumina generally produced by fusing a calcined alumina in an electric furnace such as at about 2500 to 3000°C.

The alumina in Example 1 of Kaaber is not a fused alumina, but is an alumina that remains in a cold bath. The cold bath is an electrolysis bath that was employed to produce aluminum metal from alumina. An electrolysis bath would be operated at a temperature of less than 1,000°C. Thus, the alumina in an electrolysis bath is not a fused alumina.

Applicants refer the Examiner to U.S. Patent 5,814,127 to Li et al, a copy of which is attached, which shows the temperature of operation of the electrolysis bath and in particular shows that the operation temperature of the electrolysis bath for aluminum (the Hall-Heroult process) is less than 1000°C. See column 1, lines 15 to 21.

Kaaber at column 3, lines 51 to 52 does refer to fused alumina particles, but this disclosure relates to the use of fused alumina particles as an abrasive with the grinding aid produced from the cold bath. Thus, this disclosure recognizes the difference between fused alumina particles and the alumina in the cold bath.

With respect to Kubota et al, the Examiner states at page 6 of the Office Action as follows:

Kubota, a method of modifying graphite particles, discloses using a jet mill to collide particles (column 5, lines 14 to 16) to reduce particle size to 1 to 100 pm (column 5, lines 10 to 11) and round the particles to a roundness of not less than 0.86 (column 4, lines 4 to 5). Thus both of the prior art references disclose using a jet mill to reduce particle size. Further, rounding a particle is an inherent function of the grinding. Further, Kubota specifically discloses using the jet mill to round the particles.

However, applicants submit that Kubota et al do not suggest that the use of jet mill inherently causes rounding of particles.

In particular, applicants refer the Examiner to the following descriptions of Kubota et al:

Japanese Kokai Tokkyo Koho Nos. H08-213020 and H08- 298117 (in both, the applicant being the instant applicant) disclose a method of grinding scaly natural graphite using a jet mill, with examples in which the grinding is performed using a Hosokawa Micron's Micron, jet mill or Alpine's counter jet mill. These publications contain an explanation to the effect that whereas ordinary attrition or grinding down of scaly natural graphite by friction using ball mills or the like causes fracture to a crushed and squashed state, jet mill grinding cut such graphite sharply to pieces while retaining the scaly shape. (Kubota, Column 1, lines 37 to 47)

Although the above-cited "Saishin Funryutai Process Gijutsu Shusei (Process Hen)" mentions that fluid energy type grinding gives particles having a rather round shape with corners rounded off, the description merely means that the corners of natural

graphite particles are rounded off in the category of grinding but does not mean that the particles are made spheroidal.

The description in the above-cited Japanese Kokai Tokkyo Koho H08-213020 and H08-298117 is also intended to mean that scaly natural graphite is ground in the category of grinding without loss of the scaly shape.

While it is known that scaly natural graphite particles can be ground as mentioned above, it is believed to be unknown that scaly natural graphite particles could be made spheroidal by modification processing thereof so as to bring their shape close to a spherical form.

(Kubota, Column 1, line 64 to column 2, line 13)

Based on the above knowledge, Kubota et al provide a method for producing roundish graphite particles with the use of a particular kind of milling process which is specially adopted for rounding of graphite particles.

Therefore, one of ordinary skill in the art would have never believed that the use of a jet mill inherently causes rounding of particles, and that edges of fused alumina particles are removed by making the fused alumina particles collide with each other with use of a jet mill.

In view of the above, applicants submit that Kaaber and Kubota et al do not disclose or render obvious the subject matter of claim 2 and the claims dependent thereon.

With respect to the rejections of claims 5, 7 and 15 to 17, these are dependent claims that depend from claim 2. Applicants submit that these claims are patentable for the same reasons as discussed above in connection with claim 2. Kugelberg et al, Haddow and Kanbara et al do not supply the above discussed deficiencies. Accordingly, applicants request withdrawal of these rejections.

In view of the above, applicants submit that Kaaber and Kubota et al do not disclose or render obvious the presently claimed invention and, accordingly, request withdrawal of these rejections.

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

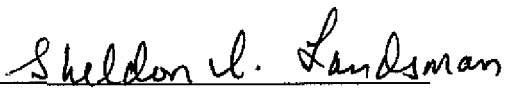
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Date: March 8, 2010


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United States Patent [19]

Li

[11] Patent Number: 5,814,127

[45] Date of Patent: Sep. 29, 1998

[54] PROCESS FOR RECOVERING CF_4 AND C_2F_6 FROM A GAS

[75] Inventor: Yao-En Li, Buffalo Grove, Ill.

[73] Assignee: American Air Liquide Inc., Walnut Creek, Calif.

[21] Appl. No.: 772,469

[22] Filed: Dec. 23, 1996

[51] Int. Cl.⁶ B01D 46/00; B01D 53/14; B01D 53/22

[52] U.S. Cl. 95/47; 95/51; 95/54; 95/131; 95/287; 423/240 R

[58] Field of Search 95/45, 47, 51, 95/54, 131, 133, 233, 286, 287; 423/240 R, 240 S

[56] References Cited

U.S. PATENT DOCUMENTS

2,947,687	8/1960	Lee	210/23
2,953,502	9/1960	Binning et al.	202/12
2,960,462	11/1960	Lee et al.	208/308
2,970,106	1/1961	Binning et al.	208/347
2,997,132	8/1961	Allander et al.	95/233 X
3,307,330	3/1967	Niedzielski et al.	95/45
3,508,994	4/1970	Nyrop	156/280
3,616,607	11/1971	Klass et al.	55/16
3,648,845	3/1972	Riley	210/490
3,792,571	2/1974	Waki et al.	95/131 X
3,827,955	8/1974	Bahri et al.	95/131 X
3,876,394	4/1975	Nix	95/131 X
4,086,310	4/1978	Bottenbruch et al.	264/41
4,113,628	9/1978	Alegranti	210/500
4,132,824	1/1979	Kimura et al.	428/516
4,155,793	5/1979	Salemme et al.	156/246
4,156,597	5/1979	Browall	55/16
4,192,824	3/1980	Robinson et al.	585/409
4,378,324	3/1983	Makino et al.	364/41
4,460,526	7/1984	Makino et al.	264/41
4,474,662	10/1984	Makino et al.	264/41
4,485,056	11/1984	Makino et al.	264/41
4,512,893	4/1985	Makino et al.	210/500
4,551,156	11/1985	Li	95/47
4,557,921	12/1985	Kirsch et al.	95/131 X

4,602,922	7/1986	Cabasso et al.	55/158
4,664,669	5/1987	Ohyabu et al.	623/66
4,681,602	7/1987	Glenn et al.	95/54 X
4,689,267	8/1987	Takamizawa et al.	428/376
4,713,292	12/1987	Takemura et al.	428/373
4,714,481	12/1987	Matsuura et al.	55/158
4,717,394	1/1988	Hayes	55/158
4,741,829	5/1988	Takemura et al.	210/500
4,756,932	7/1988	Puri	427/175
4,781,907	11/1988	McNeill	95/54 X
4,826,599	5/1989	Bikson et al.	210/500
4,833,877	5/1989	Ahland et al.	95/131 X

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

0 117 338	9/1984	European Pat. Off.
0 389 126	9/1990	European Pat. Off.
0 521 203	1/1993	European Pat. Off.
0 754 487	1/1997	European Pat. Off.

OTHER PUBLICATIONS

Database WPI, Section Ch, Week 8640, Derwent Publications Ltd., London, GB, Class A14, AN 86-260855.

Alton T. Tabereaux, Anode Effests, PFCs, Global Warming, and the Aluminum Industry, JOM, pp. 30-34 (Nov. 1994). Aluminum and Alloys, vol. 2, pp. 191-192 and 195-196.

Primary Examiner—Robert Spitzer

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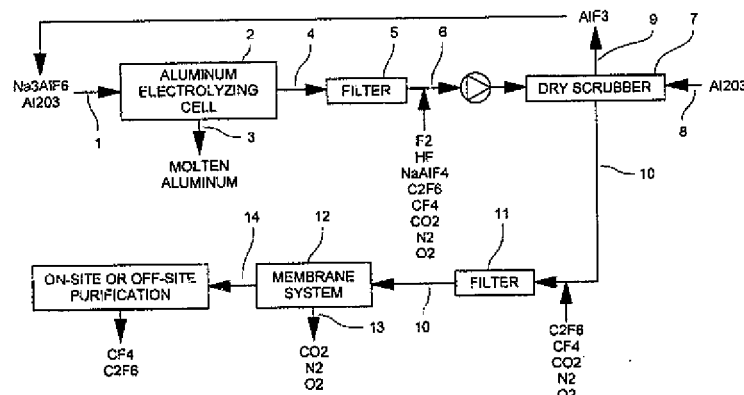
[57] ABSTRACT

A process for recovering at least one of CF_4 and C_2F_6 from a vent gas from an aluminum electrolysis cell. The process includes the steps of:

(a) removing inorganic fluorides from a vent gas comprising inorganic fluorides and at least one of CF_4 and C_2F_6 to obtain a purified vent gas; and

(b) contacting the purified vent gas with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF_4 and C_2F_6 , and a permeate stream depleted in at least one of CF_4 and C_2F_6 .

12 Claims, 3 Drawing Sheets



U.S. PATENT DOCUMENTS

4,881,953	11/1989	Prasad et al.	95/54 X	5,281,253	1/1994	Thompson	95/45 X
5,042,992	8/1991	Blinka et al.	95/51	5,282,969	2/1994	Xu	95/45 X
5,055,116	10/1991	Kohn et al.	95/47	5,310,415	5/1994	Simmons et al.	95/45
5,085,676	2/1992	Ekiner et al.	55/158	5,378,263	1/1995	Prasad	95/54
				5,391,219	2/1995	Matsumoto et al.	95/51
				5,470,379	11/1995	Garrett	95/54 X

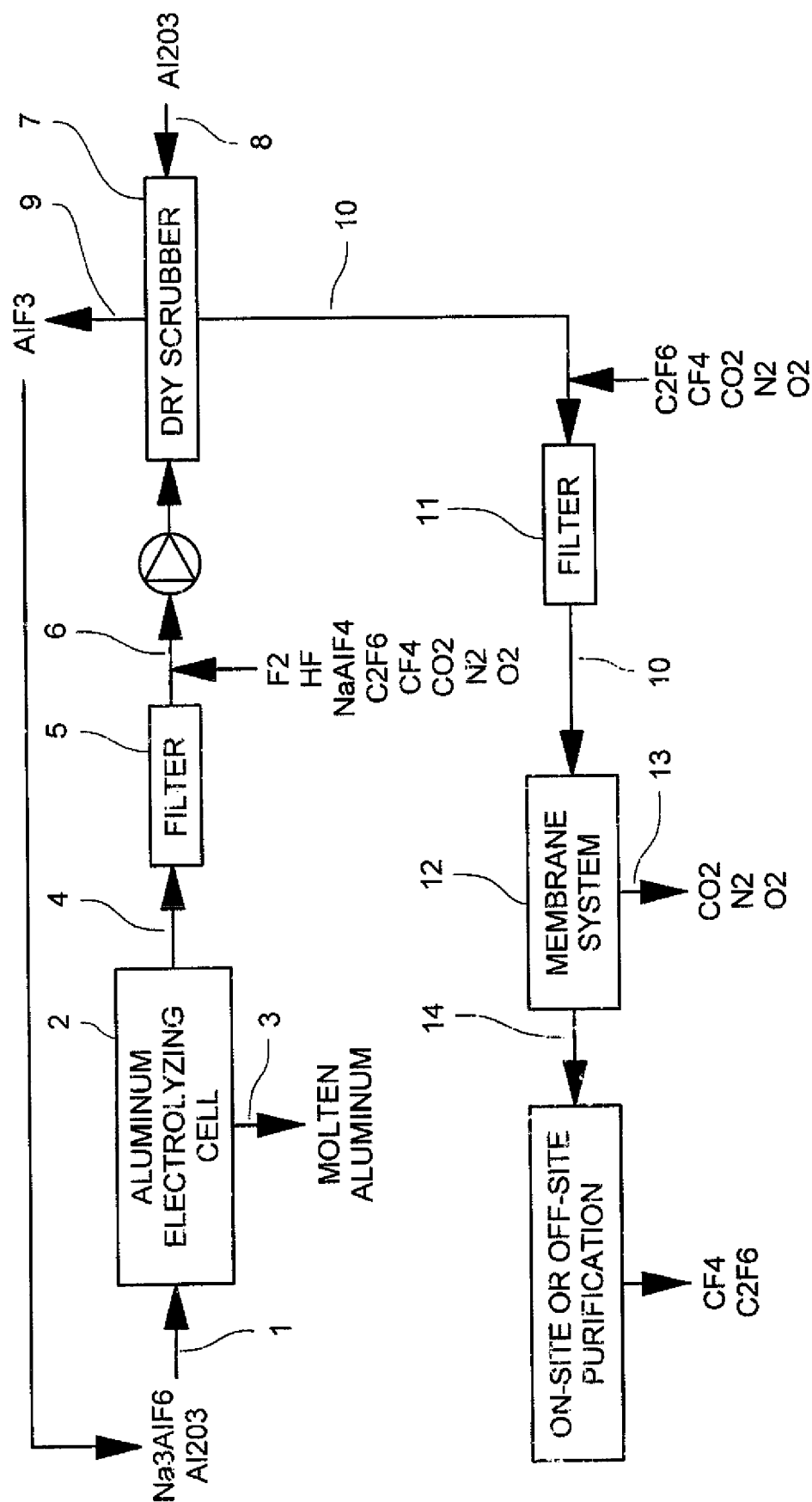
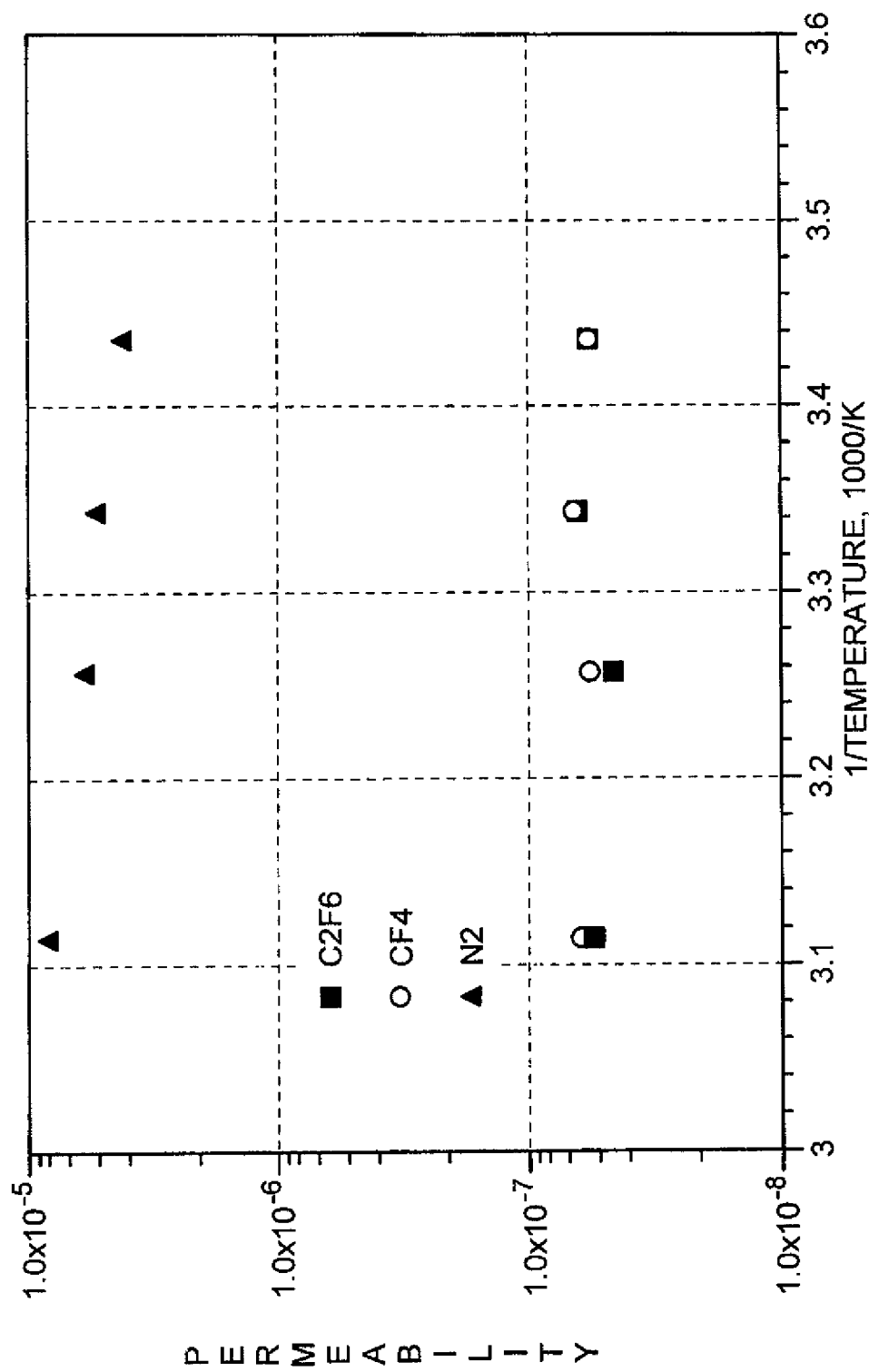


FIG. 1

PROCESS FLOW DIAGRAM FOR C₂F₆ AND CF₄ RECYCLE

**FIG. 2**PERMEABILITIES OF N₂, CF₄ AND C₂F₆ AT DIFFERENT TEMPERATURES

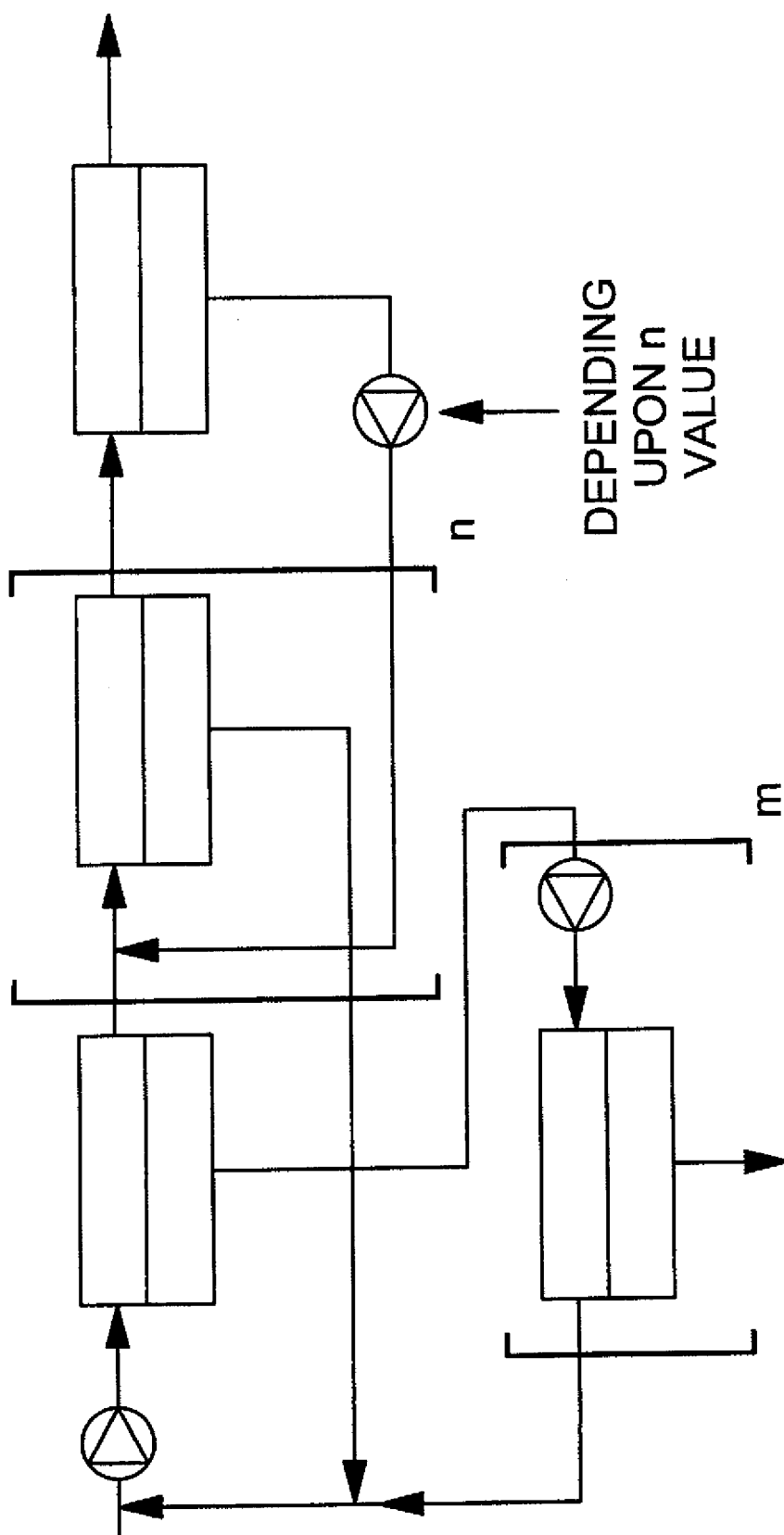


FIG. 3
ENGINEERING DESIGN OF MEMBRANE SYSTEM

PROCESS FOR RECOVERING CF₄ AND C₂F₆ FROM A GAS

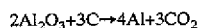
FIELD OF THE INVENTION

The present invention generally relates to a gas separation process. The invention particularly relates to a process for removing at least one of CF₄ and C₂F₆ from a gas stream using a membrane. The invention also particularly relates to a method of making aluminum, which method includes removing at least one of CF₄ and C₂F₆ from a gas stream using a membrane.

BACKGROUND OF THE INVENTION

Currently, aluminum metal is commercially manufactured in two steps. The first step involves extracting alumina (Al₂O₃) from bauxite using a Bayer process. The second step involves reducing the alumina which is dissolved in a mixture of molten cryolite (Na₃AlF₆) and aluminum trifluoride (AlF₃) in an electrolysis cell at about 950° to 960° C. using the Hall-Heroult process. In the second step, aluminum-containing ions are reduced electrochemically to produce metallic aluminum at the metal cathode surface.

During normal electrolysis, carbon anodes are consumed as oxygen-containing ions react with the carbon anodes to form carbon dioxide and aluminum metal according to the following equation:

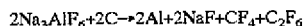


However, at certain conditions, the electrolysis cell approaches an anode effect. This approach is characterized by the following events:

- (1) The alumina concentration in the bulk of the electrolyte decreases below 2% by weight;
- (2) Higher concentrations of fluoride ions prevail near the anode as the concentration of oxygen containing ions decreases;

- (3) The anode polarization voltage increases significantly;
- (4) The critical current density of the carbon anode is exceeded for the discharge of only oxygen-containing anions; and
- (5) F₂ is eventually discharged at the anode surface from the decomposition of cryolite.

During anode effects, the fluorine discharged at the anode reacts with the carbon to form CF₄ and C₂F₆ according to the following equation:



For a more detailed discussion of the anode effect, see Alton T. Tabereaux, *Anode Effects, PFCs, Global Warming, and the Aluminum Industry*, JOM, pp. 30-34 (November 1994).

For a typical electrolysis cell, the emission rate of CF₄ and C₂F₆ per day is 0.25 kg. There are normally 100 to 200 cells per plant. Therefore, the daily emission of CF₄ and C₂F₆ per plant is about 50 kg.

The emission of CF₄ and C₂F₆ from aluminum plants has typically been vented directly into the atmosphere. However, these gases, which are 10,000 times more potent than CO₂, have recently been classified as global warming gases. Thus, with the signing of the United Nations Framework Convention on Climate Change which is aimed at reducing the emission of global warming gases, there is a significant need in the industry for a way to minimize or eliminate the emission of these gases into the atmosphere.

Accordingly, it is an object of the present invention to address this need in the aluminum industry.

These and other objects of the invention will become apparent in light of the following specification, and the appended drawings and claims.

SUMMARY OF THE INVENTION

The present invention relates to a process for recovering at least one of CF₄ and C₂F₆ from a vent gas from an aluminum electrolysis cell. The process comprises the steps of:

(a) removing inorganic fluorides from a vent gas comprising inorganic fluorides and at least one of CF₄ and C₂F₆ to obtain a purified vent gas; and

(b) contacting the purified vent gas with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF₄ and C₂F₆, and a permeate stream depleted in at least one of CF₄ and C₂F₆.

In another aspect, the present invention relates to a method of making aluminum. The method includes the steps of:

(a) electrolytically reducing alumina dissolved in a mixture of molten cryolite and aluminum trifluoride in an electrolysis cell to produce aluminum;

(b) withdrawing a vent gas comprising F₂, HF, and at least one of CF₄ and C₂F₆ from the electrolysis cell;

(c) contacting the vent gas with alumina at conditions effective to react F₂ and HF with the alumina to produce aluminum trifluoride and a gas stream comprising the at least one of CF₄ and C₂F₆;

(d) recycling at least a portion of the aluminum trifluoride from step (c) to the electrolysis cell; and

(e) contacting the gas stream comprising the at least one of CF₄ and C₂F₆ with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF₄ and C₂F₆, and a permeate stream depleted in at least one of CF₄ and C₂F₆.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a process flow diagram for recovering CF₄ and C₂F₆ according to the present invention.

FIG. 2 is a graph showing the relative permeabilities of N₂, CF₄, and C₂F₆ through a particular membrane at different temperatures.

FIG. 3 illustrates an engineering design of a membrane system that can be employed in the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In its broadest aspect, the present invention relates to a process for removing at least one of CF₄ and C₂F₆ from a gas stream. Preferably, the present invention relates to a process for removing both CF₄ and C₂F₆ from a gas stream containing the same.

Prior to separation, the gas stream preferably contains from about 0.01 to about 20% by volume of at least one of CF₄ and C₂F₆. In addition to containing at least one of CF₄ and C₂F₆, the gas stream can include oxygen, carbon dioxide, and nitrogen as well as other gaseous components.

The process according to the present invention comprises the step of contacting the gas stream with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF₄ and C₂F₆, and a permeate stream depleted in at least one of CF₄ and C₂F₆. Preferably, the retentate stream is depleted in oxygen, carbon dioxide, and nitrogen while the permeate stream is rich in oxygen, carbon dioxide,

and nitrogen. If both CF_4 and C_2F_6 are present in the gas stream, then the contacting step preferably produces a retentate stream rich in both CF_4 and C_2F_6 , and a permeate stream depleted in both CF_4 and C_2F_6 .

As used in this specification and the claims, the term "rich" means that the concentration of a particular component in that stream is greater than the concentration of the same component in the feed stream. Likewise, the term "depleted" means that the concentration of a particular component in that stream is less than the concentration of the same component in the feed stream.

The retentate stream preferably comprises from about 25 to about 100% by volume of at least one of CF_4 and C_2F_6 . The permeate stream preferably comprises from about 0 to about 0.01% by volume of at least one of CF_4 and C_2F_6 .

In a preferred embodiment, the purity of the permeate and retentate streams is improved by contacting the streams with additional membranes arranged in series. Such a process may be carried out according to the multi-step membrane separation system shown in FIG. 3. As shown in FIG. 3, each of the permeate and retentate streams may be passed to another membrane contacting unit to increase the purity of the stream. The number of contacting steps "m" and "n" may vary depending on the purity desired. By using such a process, it is possible to obtain 100% recovery of at least one of CF_4 and C_2F_6 with a purity approaching 100%.

Any membrane can be used in the process according to the present invention so long as the membrane can selectively retain at least one of CF_4 and C_2F_6 while passing the other components in the gas stream through. The membrane should also be substantially non-reactive with the gaseous components to be separated.

Membranes useful in the invention are preferably glassy membranes such as polymer membranes made preferably from polyimides; polyamides; polyamide-imides; polyesters polycarbonates; polysulfones; polyethersulfone; polyetherketone; alkyl substituted aromatic polyesters; blends of polyethersulfone, aromatic polyimides, aromatic polyamides, polyamides-imides, fluorinated aromatic polyimide, polyamide, and polyamide-imides; glassy polymeric membranes such as those disclosed in U.S. Ser. No. 08/247,125 filed May 20, 1994, (now abandoned) the content of which is hereby incorporated by reference; cellulose acetates; and blends thereof, copolymers thereof, substituted polymers (e.g. alkyl, aryl) thereof and the like.

Asymmetric membranes are prepared by the precipitation of polymer solutions in solvent-miscible nonsolvents. Such membranes are typified by a dense separating layer supported on an anisotropic substrate of a graded porosity and are generally prepared in one step. Examples of such membranes and their methods of manufacture are disclosed in U.S. Pat. Nos. 4,113,628; 4,378,324; 4,460,526; 4,474,662; 4,485,056; 4,512,893; 5,085,676; and 4,717,394; all incorporated herein by reference. The '394 and '676 patents disclose preparation of asymmetric separation membranes from selected polyimides. Particularly preferred membranes are polyimide asymmetric gas separation membranes as disclosed in the '676 patent.

In a pressure driven gas membrane separation process, one side of the gas separation membrane is contacted with a complex multicomponent gas mixture and certain of the gases of the mixture permeate through the membrane faster than the other gases. Gas separation membranes thereby allow some gases to permeate through them while serving as a barrier to other gases in a relative sense. The relative gas permeation rate through the membrane is a property of the

membrane material composition and its morphology. It has been suggested in the prior art that the intrinsic permeability of a polymer membrane is a combination of gas diffusion through the membrane, controlled in part by the packing and molecular free volume of the material, and gas solubility within the material. Selectivity is the ratio of the permeabilities of two gases being separated by a material. It is also highly desirable to form defect-free dense separating layers in order to retain high gas selectivity.

Composite gas separation membranes typically have a dense separating layer on a preformed microporous substrate. The separating layer and the substrate are usually different in composition. Composite gas separation membranes have evolved to a structure of an ultrathin, dense separating layer supported on an anisotropic, microporous substrate. These composite membrane structures can be prepared by laminating a preformed ultrathin dense separating layer on top of a preformed anisotropic support membrane. Examples of such membranes and their methods of manufacture are disclosed in U.S. Pat. Nos. 4,664,669; 4,689,267; 4,741,829; 2,947,687; 2,953,502; 3,616,607; 4,714,481; 4,602,922; 2,970,106; 2,960,462; 4,713,292; 4,086,310; 4,132,824; 4,192,824; 4,155,793; and 4,156,597; all incorporated herein by reference.

Alternatively, composite gas separation membranes may be prepared by multistep fabrication processes, wherein first an anisotropic, porous substrate is formed, followed by contacting the substrate with a membrane-forming solution. Examples of such methods are described in U.S. Pat. Nos. 4,826,599; 3,648,845; and 3,508,994; all incorporated herein by reference.

U.S. Pat. No. 4,756,932 describes how composite hollow-fiber membranes may also be prepared by co-extrusion of multiple polymer solution layers, followed by precipitation in a solvent-miscible nonsolvent.

According to one embodiment of the present invention, the membrane can be post-treated with, or coated by, or coextruded with, a fluorinated or perfluorinated polymer layer in order to increase its ability to withstand harmful constituents in the gas mixture from which PFCs are to be separated, at low levels or temporary contact with such components.

The hollow-fiber spinning process depends on many variables which may affect the morphology and properties of the hollow-fiber membrane. These variables include the composition of the polymer solution employed to form the fiber, the composition of fluid injected into the bore of the hollow-fiber extrudate during spinning, the temperature of the spinneret, the coagulation medium employed to treat the hollow-fiber extrudate, the temperature of the coagulation medium, the rapidity of coagulation of the polymer, the rate of extrusion of the fiber, takeup speed of the fiber onto the takeup roll, and the like.

The temperature of the gas mixture and/or the membrane during the contacting step can vary from about -10°C . to about 100°C . Preferably, the temperature is between about 10°C . and 80°C . More preferably, the temperature ranges from ambient, i.e., from about 20°C . to 25°C ., to about 60°C .

It is preferred, according to the present invention, to have a pressure drop across the membrane of less than about 2,000 psig. More preferably, the pressure drop ranges from about 3 to about 200 psig. Even more preferably, the pressure drop is about 20 to about 60 psig.

The requisite pressure drop across the membrane can be provided in one of two ways. First, the feed gas stream can

be compressed. Preferred compressors are sealed and oil-free, such as the compressors sold under the tradename POWEREX, available from the Powerex Harrison Company of Ohio. Second and more preferably, the pressure drop across the membrane can be established by lowering the pressure on the permeate side of the membrane. To create the lower pressure on the permeate side, a vacuum pump or any other suction device can be used.

The flowrate of the gas stream across the membrane can vary from about 0 to about 10^5 Nm³/h per square meter of membrane available for separation. Preferably, the flowrate is from about 10^{-4} to about 10 Nm³/h-m². More preferably, the flowrate is from about 0.1 to about 0.5 Nm³/h-m².

In a preferred aspect, the present invention relates to a process for recovering at least one of CF₄ and C₂F₆ from a vent gas from an aluminum electrolysis cell. The vent gas comprises (1) gaseous components such as O₂, CO₂, and N₂; (2) inorganic fluorides such as F₂, HF, and NaAlF₄; and (3) at least one of CF₄ and C₂F₆. The vent gas can also include some hydrocarbons and a large amount of particulates.

The first step in this process involves removing the inorganic fluorides from the vent gas to produce a purified vent gas. The inorganic fluorides are preferably removed from the vent gas by using a caustic scrubber. The scrubber can be wet or dry. Dry scrubbers are usually resin-type scrubbers or soda-lime, while some dry scrubbers comprising catalysts such as MnO₂ can also be used. Exemplary wet scrubbers that can be used in the present invention are described in the brochure entitled, "Selecting a CDO™ for Your Particular Application" from DELATECH Corporation, which brochure is hereby incorporated by reference. When various harmful constituents have to be removed, it is preferred to use a dry scrubber or scrubbers in series with a wet scrubber or scrubbers.

Preferably, upstream of the scrubber or scrubbers, one or more filters are employed to remove the particulates from the vent gas. It is preferred to use a filter having a pore size diameter of less than 20 micrometers, and more preferably, less than 10 micrometers.

The second step in this process involves contacting the purified vent gas with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF₄ and C₂F₆, and a permeate stream depleted in at least one of CF₄ and C₂F₆. This membrane separation step can be carried out as described above.

If there are remaining particulates in the purified vent gas before it is passed to the membrane separation unit, it is contemplated by the present invention to employ an additional filter or filters to remove such particulates.

In another preferred aspect, the present invention relates to a method of making aluminum. The method includes the steps of:

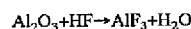
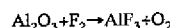
- (a) electrolytically reducing alumina dissolved in a mixture of molten cryolite and aluminum trifluoride in an electrolysis cell to produce aluminum;
- (b) withdrawing a vent gas comprising F₂, HF, and at least one of CF₄ and C₂F₆ from the electrolysis cell;
- (c) contacting the vent gas with alumina at conditions effective to react F₂ and HF with the alumina to produce aluminum trifluoride and a gas stream comprising the at least one of CF₄ and C₂F₆;
- (d) recycling at least a portion of the aluminum trifluoride from step (c) to the electrolysis cell; and
- (e) contacting the gas stream comprising the at least one of CF₄ and C₂F₆ with a membrane at conditions effective to

obtain a retentate stream rich in at least one of CF₄ and C₂F₆, and a permeate stream depleted in at least one of CF₄ and C₂F₆.

The general features of this method are illustrated in FIG. 1. Referring to FIG. 1, a stream 1 of alumina, cryolite, and aluminum trifluoride is fed into an aluminum electrolyzing cell 2 where molten aluminum is produced by electrolytically reducing the alumina. The operating conditions and equipment necessary to carry out this step are well known to those skilled in the art.

The molten aluminum is then withdrawn from the electrolyzing cell 2 through line 3. A vent gas stream 4 is also withdrawn from the electrolyzing cell 2. The vent gas stream 4 comprises O₂, CO₂, N₂, F₂, HF, NaAlF₄, CF₄, C₂F₆, and particulates. The vent gas stream 4 is optionally passed to a filter 5 to remove the particulates therein.

A filtered vent gas 6 is optionally withdrawn from filter 5 and passed to a dry scrubbing zone 7. In the scrubbing zone 7, the filtered vent gas 6 is contacted with alumina introduced through line 8 at conditions effective to remove inorganic fluorides such as F₂ and HF therefrom. These conditions for carrying out this scrubbing step are well known to those skilled in the art. During the scrubbing step, the alumina reacts with F₂ and HF in the filtered vent gas 6 to form aluminum trifluoride according to the following equations:



A stream 9 comprising the aluminum trifluoride is then withdrawn from the dry scrubbing zone 7 and recycled to stream 1. The dry scrubbing zone 7 also yields a purified vent gas stream 10 containing CF₄, C₂F₆, O₂, CO₂, and N₂. Stream 10 is passed to an additional filter 11, if necessary, to remove any remaining particulates therein. The purified vent gas stream 10 is next passed to a membrane separation system 12 such as the one described above and illustrated in FIG. 3 where a retentate stream 14 and a permeate stream 13 are produced. The permeate stream 13 comprises mostly of O₂, CO₂, and N₂, while the retentate stream 14 comprises mostly of CF₄ and C₂F₆. The retentate stream 14 comprising CF₄ and C₂F₆ may be further purified on or off-site to produce a CF₄/C₂F₆ stream suitable for use in the semiconductor industry.

EXAMPLES

The following examples are provided to illustrate the present invention and are not to be construed as a limitation thereof.

Example 1

A gas stream comprising CF₄, C₂F₆, and N₂ was contacted with a polyimide, asymmetric composite hollow fiber membrane at various temperatures to measure the relative permeabilities of CF₄, C₂F₆, and N₂. The gas stream had a constant flowrate rate of 170 sccm. The pressure of the feed gas was kept constant at 3 bar. The permeabilities of each of these components are graphically shown in FIG. 2. As seen from FIG. 2, the selectivities of CF₄/N₂ and C₂F₆/N₂ are on the order of 300.

Based on the above selectivities, a computer simulation of a single stage membrane separation unit was conducted. The concentration and pressure of the feed, permeate, and reten-

tate as well as the $\text{CF}_4/\text{C}_2\text{F}_6$ recovery are shown in Table 1 below.

TABLE 1

	Feed	Permeate	Retentate	$\text{CF}_4/\text{C}_2\text{F}_6$ Recovery
Flowrate (Nm_3/h)	10	9.7	0.3	
$[\text{CF}_4]$ (vol %)	0.1	1.2×10^{-3}	3.9	
$[\text{C}_2\text{F}_6]$ (vol %)	0.1	1.5×10^{-3}	3.9	
Pressure (bar)	20	0.2	19.7	
				98.7%

Example 2

The procedure of Example 1 was repeated using the feed concentration and pressure listed in Table 2 below. The simulated results are also listed in Table 2.

TABLE 2

	Feed	Permeate	Retentate	$\text{CF}_4/\text{C}_2\text{F}_6$ Recovery
Flowrate (Nm_3/h)	10	9.4	0.6	
$[\text{CF}_4]$ (vol %)	1.0	0.04	16.5	
$[\text{C}_2\text{F}_6]$ (vol %)	5.0	0.16	83.1	
Pressure (bar)	30	0.2	29.7	
				96.9%

Example 3

For a typical smelting plant with 100 smelting pots, the flowrate of the vent gas is about $3 \text{ Nm}^3/\text{h}$. The same procedure of Example 1 was followed using such a stream. The feed concentration and pressure as well as the simulated results of such a stream are reported in Table 3 below.

TABLE 3

	Feed	Permeate	Retentate	$\text{CF}_4/\text{C}_2\text{F}_6$ Recovery
Flowrate (Nm_3/h)	3	2.6	0.4	
$[\text{CF}_4]$ (vol %)	10.0	0.2	79.2	
$[\text{C}_2\text{F}_6]$ (vol %)	1.0	0.02	7.9	
Pressure (bar)	10	1.0	9.7	
				98.1%

Example 4

In an actual experiment, a feed stream comprising 1.14% CF_4 and C_2F_6 , and the balance N_2 was contacted with a polyimide, asymmetric composite hollow fiber membrane at room temperature. The flowrate, concentration, and pressure of the feed, permeate, and retentate streams along with the percentage recovery of CF_4 and C_2F_6 are reported in Table 4 below.

TABLE 4

	Feed	Permeate	Retentate	$\text{CF}_4/\text{C}_2\text{F}_6$ Recovery
Flowrate (scfh)	313.8	310	3.8	
$[\text{CF}_4]$ (vol %)	0.45	<0.001	37.7	
$[\text{C}_2\text{F}_6]$ (vol %)	0.69	0.003	57.9	
Pressure (bar)	7.8	1.0	7.7	
				99.999%

While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

What is claimed is:

1. A process for recovering at least one of CF_4 and C_2F_6 from a vent gas from an aluminum electrolysis cell, said process comprising the steps of:

(a) removing inorganic fluorides from a vent gas comprising inorganic fluorides and at least one of CF_4 and C_2F_6 to obtain a purified vent gas; and

(b) contacting said purified vent gas with a membrane at conditions effective to obtain a retentate stream rich in at least one of CF_4 and C_2F_6 , and a permeate stream depleted in at least one of CF_4 and C_2F_6 .

2. The process according to claim 1, wherein said inorganic fluorides are F_2 , HF , and NaAlF_4 .

3. The process according to claim 1, wherein step (a) is carried out using a caustic scrubber.

4. The process according to claim 1, wherein said vent gas further comprises particulates, and wherein said vent gas is contacted with a filter to remove said particulates prior to step (a).

5. The process according to claim 1, wherein said purified vent gas further comprises particulates, and wherein said purified vent gas is contacted with a filter to remove said particulates prior to step (b).

6. The process according to claim 1, wherein said vent gas comprises both CF_4 and C_2F_6 , and said retentate stream is rich in both CF_4 and C_2F_6 , and said permeate stream is depleted in both CF_4 and C_2F_6 .

7. The process according to claim 1, wherein said vent gas further comprises O_2 , CO_2 , and N_2 .

8. The process according to claim 7, wherein said retentate stream is depleted in O_2 , CO_2 , and N_2 , and said permeate stream is rich in O_2 , CO_2 , and N_2 .

9. The process according to claim 1, wherein said vent gas comprises from about 0.01 to about 20% by volume of at least one of CF_4 and C_2F_6 .

10. The process according to claim 9, wherein said retentate stream comprises from about 25 to about 100% by volume of at least one of CF_4 and C_2F_6 , and said permeate stream comprises from about 0 to about 0.01% by volume of at least one of CF_4 and C_2F_6 .

11. The process according to claim 1, wherein said conditions comprise a temperature between about 10° and about 80°C ., a pressure drop between about 3 and about 200 psig, and a flowrate rate between about 10^{-4} and about $10 \text{ Nm}^3/\text{h-m}^2$.

12. The process according to claim 1, wherein said membrane is selected from the group consisting of polyimides, polyamides, polyamide-imides, polyesters, polycarbonates, polysulfones, polyethersulfone, polyetherketone, alkyl substituted aromatic polyesters, and

blends of polyethersulfone, aromatic polyimides, aromatic polyamides, polyamides-imides, fluorinated aromatic polyimide, polyamide, and polyamide-imides.

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